Theoretical analysis of multinary nitride semiconductors by density functional theory

T. Misaki, X-P. Wu, A. Wakahara, and A. Yoshida
Dept. of Electrical and Electronic Eng., Toyohashi University of Technology, Toyohashi 441-8580, Japan
Tel:+81-532-44-6742, Fax:+81-532-44-6757, e-mail:misaki@yoshi2.dev.eee.tut.ac.jp

1. Introduction

A new set of nitride semiconductors, expressed as II-IV-N_2 compound system, has led to a growing interest to extensive experimental efforts. II-IV-N_2 compound system is derived from III-V compounds[1]. The transfer from III-V to II-IV-V_2 compounds brings new properties of the materials, such as band structure, band gap, and non-linear optical properties. However, few investigations have been made on II-IV-N_2 compounds[2),3)], and thus, the fundamental properties of these materials are not clear till now.

First principle calculation is powerful tool for searching new materials, which have wide band gap with small lattice mismatch to group-III nitrides, because it is very difficult to synthesize and investigate all kinds of new materials.

In this paper, fundamental properties of multinary nitride semiconductors have investigated by means of first principle calculations based on the density functional theory.

2. Structure and calculation methods

On the calculations, Mg, Ca, Zn and Cd were chosen as group-II elements and Si, Ti, Ge and Zr were chosen group-IV elements. An orthorhombic structure with the space group of $Pna2_1$, which is wurtzite-like structure and reported for $ZnGeN_2$ and $MgSiN_2$, was used for the investigation(Fig.1) [4)-6)].

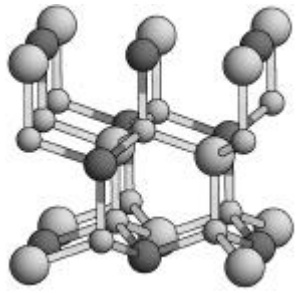
Total energy calculation was carried out by using the density functional theory with generalized gradient approximation(GGA)[7),8)]. A plane wave basis with the cut-off energy of 500 eV was used to explain the wave function, and the structural optimization was achieved by minimizing the total energy under the preconditioned configuration.

3. Results and discussion

For $Pna2_1$ structure, atom arrangement of (001) surface has a hexagonal-like surface lattice like a wurtzite structure, such GaN. Among the treated II-IV-N_2 systems, $(Mg_xZn_{1-x})(Si_yGe_{1-y})N_2$ are close to those of GaN, and thus, we focused on the properties of $(Mg_xZn_{1-x})(Si_yGe_{1-y})N_2$. In order to see the lattice mismatch between GaN and calculated II-IV-N_2 compounds, the calculated lattice parameters were redefined as quasi-wurtzite structure by using averaged hexagonal lattice parameter *a*. The redefined lattice parameters and the band gap energies of $(Mg_xZn_{1-x})(Si_yGe_{1-y})N_2$ are summarized in Table 1.

The lattice constants of $ZnGeN_2$ are a = 3.144 Å and c = 6.367 Å, which is similar to experimental values of a = 3.186 Å and c = 5.174 Å[4)]. The lattice mismatch between GaN and $ZnGeN_2$ is +1.40 %. Fig.2 shows a possible atom arrangement of $ZnGeN_2$ on GaN (0001). The lattice constants of the other materials are also close to those of $ZnGeN_2$. Therefore, $(Mg_xZn_{1-x})(Si_yGe_{1-y})N_2$ system can be epitaxially grown on both GaN and SiC.

The predicted band structure of $ZnGeN_2$ is a direct transition at Γ point with the gap energy of 2.65 eV(Fig.3), which agrees well with experimental value of 2.67 eV[9)]. The band gap energy of $ZnGeN_2$ corresponds to the middle of the blue region of the spectrum. On the other hand, the predicted band structure



Orthorhombic ($Pna2_1$)

Fig. 1. Structure models used in the present work. Smallest, dark medium, and light largest spheres indicate N, group-II, and group-IV atoms.

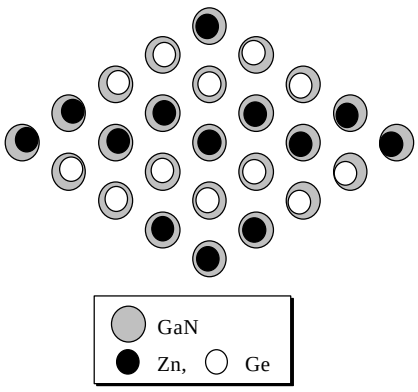


Fig. 2. Possible epitaxial relation of $ZnGeN_2$ (001) with $Pna2_1$ structure on GaN (0001) surface.

Table 1. The calculated structural parameters of multinary nitride semiconductors.

Space Group	System	Lattice Constant		Transition Type	E_g [eV]	Lattice Mismatch	
		a [Å]	*c* [Å]			GaN	SiC
$Pna2_1$	$ZnGeN_2$	3.144	6.367	direct	2.65	+1.40%	-2.00%
	$ZnSiN_2$	3.055	6.222	indirect	3.63	+4.35%	+0.85%
	$MgSiN_2$	3.126	6.461	indirect	4.31	+1.98%	-1.44%
	$MgGeN_2$	3.215	6.595	indirect	3.48	-0.84%	-4.17%

*Lattice constant *a* is defined as averaged value of atomic distance between group-II and group-IV lattice site on (001) surface.

of $MgSiN_2$ is an indirect transition. The bottom of the conduction band is located at Γ point, but the top of the valence band is located at U point. The band gap energy of 4.31 eV agree well with experimental value of 4.8 eV[10]. The transition type of $MgGeN_2$ and $ZnSiN_2$ is the same as $MgSiN_2$.

Detailed results, such as effective mass and optical properties will be presented at the workshop.

4. Conclusions

First principles calculations for II-IV-N_2 compound system have been carried out. The results of lattice constants and band gap energies of $(Mg_xZn_{1-x})(Si_yGe_{1-y})N_2$ system agreed with experimental values. It has been found that the lattice constant of $(Mg_xZn_{1-x})(Si_yGe_{1-y})N_2$ was close to that of AlN, GaN, and SiC.

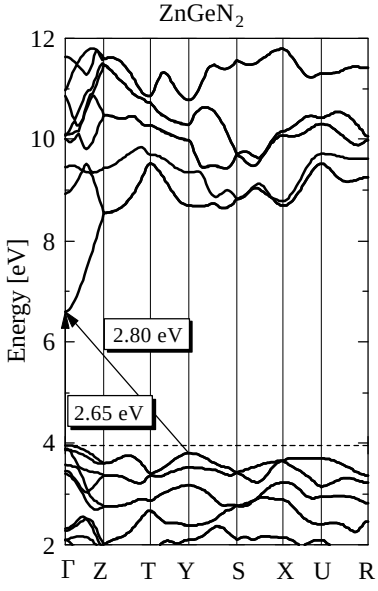


Fig. 3. The band structure of $ZnGeN_2$

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